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13. ABSTRACT (Maximum 200 words) Silicones are effective as non-toxic fouling release marine coatings, but inorganic fillers are usually used to improve their strength. The objective of this program was to develop a means of improving the strength of silicones that maintains their optical clarity for sensor applications. Hydrosilylation of hydride-terminated polydimethylsiloxane with polybutadiene in dilute solution yielded polysiloxane side-loops. Crosslinking took place on removal of solvent. When the ratio of silane to olefin in the hydrosilylation mixture was increased, the inherent viscosity of the solutions decreased drastically. The results are explained on the basis of diminishing availability of olefin sites as the reaction proceeds. When one end of a difunctional silane attaches to an olefin site and no other olefin sites are available nearby, molecular motion eventually brings a remote olefin site in the molecule into proximity. Hydrosilylation then results in permanent ring folding.				
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FINAL REPORT

CONTRACT #: NO0014-96-C-0100

PRINCIPAL INVESTIGATOR: Kurt Baum

INSTITUTION: Fluorochem, Inc.

CONTRACT TITLE: Non-Fouling Materials for Submerged Sensors

AWARD PERIOD: 6 May 1996 - 21 July 1998

OBJECTIVE: The most effective non-toxic fouling release marine coatings that have been reported are silicones. Silicones are relatively weak polymers, and inorganic fillers are usually used to improve their strength. These fillers make silicones unsuitable for use as coatings for optical sensors and similar applications. The objective of this program was to develop a means of improving the strength of silicones that maintains their optical clarity. Also, contact angle measurements have indicated migration of siloxane groups to the surface of films in air and to the interior on water immersion. Prevention of this migration is desirable.

APPROACH: High molecular weight polybutadiene was used as a molecular level reinforcement for silicones. Difunctional hydride-terminated polydimethylsiloxane was added to the double bonds of polybutadiene by hydrosilylation. To avoid premature crosslinking, the reaction was carried out in dilute solution.

ACCOMPLISHMENTS: Hydrosilylation of hydride-terminated polydimethylsiloxane with polybutadiene in dilute solution yielded polysiloxane side-loops on a hydrocarbon base, a novel polymer architecture. When films were prepared by evaporating solvent, crosslinking took place because of the increased concentration of unreacted hydrosilane and olefin groups. When the ratio of silane to olefin in the hydrosilylation mixture was increased, the inherent viscosity of the solutions decreased drastically, and properties of films changed from tough rubbers to tacky materials. Contact angle measurements of side-loop adducts show temporal stability, indicating that the tendency of polydimethylsiloxane side chains to migrate to or away from the surface, depending on the medium, is circumvented by anchoring both ends of the polydimethylsiloxane chains.

CONCLUSIONS: For adducts with low hydride to olefin ratios, the results are explained on the basis of the formation of side-loops when attachment takes place between nearby olefin groups. The decreases in solution viscosity and film strength as the hydride-to-olefin ratio is increased is rationalized on the basis of diminishing availability of olefin sites as the reaction proceeds. When one end of a difunctional silane attaches to an olefin site and no other olefin sites are available nearby, molecular motion eventually brings a remote olefin site in the molecule into proximity. Hydrosilylation then results in

permanent ring folding. Subsequent hydrosilylations can then result in a dendrimer-like globular molecule.

SIGNIFICANCE: Dendrimers are usually constructed layer by layer by a multi-step sequence starting with a polyfunctional core. Potentially, a variety of polymers with multiple reactive sites can be "stitched" with an appropriate difunctional reagent into dendrimer-like globular molecules, in a one-step reaction.

PATENT INFORMATION: Patents have been issued covering reactions of hydride terminated polysiloxanes with polybutadiene and other polyunsaturated polymers.

PUBLICATIONS AND ABSTRACTS

1. Baum, K.; Baum, J. C.; Ho, Tai J. Am. Chem. Soc. 1998, 120, 2993-2996. Side-Loop Polymers Based on the Hydrosilylation of Polybutadiene.
2. Baum, K., U. S. Patent 5,703,163, December 30, 1997. Loop Polymers.
3. Baum, K., U. S. Patent 5,811,193, September 22, 1998. Loop Polymers.